

THE CLAIMS

What is claimed is:

1. A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including at least one metalloamide source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, alkylsilyl; and x is the oxidation state on metal M.

2. The CVD precursor composition according to claim 1, wherein R¹ and R² are methyl.
3. The CVD precursor composition according to claim 1, wherein R¹ and R² are ethyl.
4. The CVD precursor composition according to claim 1, wherein M is Zr.
5. The CVD precursor composition according to claim 1, wherein M is Hf.
6. The CVD precursor composition according method according to claim 1, wherein the metalloamide source reagent compound is selected from the group consisting of: Zr(NMe₂)₄, Zr(NEt₂)₄, Ta(NEt₂)₅, Ta(NMeEt)₅, Zr(NiPr₂)₄, Zr(NMe₂)₂(NPr₂)₂, Zr(NC₆H₁₂)₄, Zr(NEt₂)₂(NPr₂)₂, Hf(NEt₂)₄, Hf(NMe₂)₄, La(NMe₂)₃, La(NEt₂)₃, Al(NMe₂)₃, Al(NEt₂)₃, Al₂(μ-NMe₂)₂(NMe₂)₄, Y(NMe₂)₃, Y(NEt₂)₃, Ti(NMe₂)₄, Ti(NEt₂)₄, Ta(NMe₂)₅, Ta(NEt₂)₅.
7. The CVD precursor composition according to claim 1, wherein the metalloamide source reagent compound is selected from the group consisting of Zr(NMe₂)₄, Zr(NEt₂)₄, Hf(NMe₂)₄ and Hf(NEt₂)₄.
8. The CVD precursor composition according to claim 1, wherein the precursor composition further comprises a solvent medium selected from the group consisting of: ethers, glymes,

tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

9. The CVD precursor composition according to claim 7, wherein the precursor composition further comprises a solvent medium selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

10. The CVD precursor composition according to claim 9, wherein the solvent is octane.

11. The CVD precursor composition according to claim 1, wherein the metalloamide source reagent compound is injected by liquid delivery into a chemical vapor deposition chamber.

12. The CVD precursor composition according to claim 1, wherein the metalloamide source reagent compounds is delivered by bubbler into a chemical vapor deposition chamber.

13. The method of claim 1 wherein the precursor composition further comprises an aminosilane source reagent compound of the formula:



wherein H is hydrogen; x is from 0 to 3; Si is silicon; N is nitrogen; each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, and C₁-C₈ perfluoroalkyl.

14. The CVD precursor composition according to claim 13, wherein the metalloamide source reagent compound and the aminosilane source reagent compound are injected by liquid delivery into a chemical vapor deposition chamber.

15. The CVD precursor composition according to claim 13, wherein the metalloamide source reagent compound and the aminosilane source reagent compound are delivered by bubbler into a chemical vapor deposition chamber.

16. The CVD precursor composition according to claim 1, wherein the precursor composition comprises multiple metalloamide source reagent compounds.

17. The CVD precursor composition according to claim 13, wherein the precursor composition further comprises a solvent medium selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

18. The CVD precursor composition according to claim 13, wherein the metalloamide source reagent compounds are co-injected by liquid delivery into a chemical vapor deposition chamber.

19. The CVD precursor composition according to claim 1, wherein the precursor composition further comprises a solvent medium selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

20. The CVD precursor composition according to claim 1, wherein the metalloamide source reagent compound is dissolved or suspended in a solvent, wherein the solvent is selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

21. A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including at least one source reagent compound of the formula:



wherein H is hydrogen; x is from 0 to 3; Si is silicon; N is nitrogen; each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, and C₁-C₈ perfluoroalkyl.

22. The CVD precursor composition according to claim 21, wherein R¹ and R² are methyl.

23. The CVD precursor composition according to claim 21, wherein R¹ and R² are ethyl.

24. The CVD precursor composition according to 21, wherein the aminosilane source reagent compound is selected from the group consisting of: Si(NMe₂)₄, and Si(NEt₂)₄.

25. The CVD precursor composition according to claim 24, wherein the precursor composition further comprises a solvent medium selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

26. The CVD precursor composition according to claim 25, wherein the solvent is octane.

27. The CVD precursor composition according to claim 21, wherein the aminosilane source reagent compound is dissolved or suspended in a solvent, wherein the solvent is selected from the group consisting of: ethers, glymes, tetraglymes, amines, polyamines, alcohols, glycols, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, cyclic ethers and combinations of two or more of the foregoing.

28. The CVD precursor composition according to claim 21, wherein the aminosilane source reagent compound is injected by liquid delivery into a chemical vapor deposition chamber.

29. The CVD precursor composition according to claim 21, wherein the aminosilane source reagent compounds is delivered by bubbler into a chemical vapor deposition chamber. Add to spec.

30. The CVD precursor of claim 21, wherein the precursor composition further comprises a metalloamide source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈.

31. The CVD precursor composition according to claim 30, wherein R¹ and R² are methyl.

32. The CVD precursor composition according to claim 30, wherein R¹ and R² of the metalloamide source reagent compound are ethyl.

33. The CVD precursor composition according to claim 30, wherein M is Zr.

34. The CVD precursor composition according to claim 30, wherein M is Hf.
35. The CVD precursor composition according to claim 30, wherein the metalloamide source reagent compound is selected from the group consisting of: $\text{Zr}(\text{NMe}_2)_4$, $\text{Zr}(\text{NEt}_2)_4$, $\text{Ta}(\text{NEt}_2)_5$, $\text{Ta}(\text{NMeEt})_5$, $\text{Zr}(\text{NiPr}_2)_4$, $\text{Zr}(\text{NMe}_2)_2(\text{NPr}_2)_2$, $\text{Zr}(\text{NC}_6\text{H}_{12})_4$, $\text{Zr}(\text{NEt}_2)_2(\text{NPr}_2)_2$, $\text{Hf}(\text{NEt}_2)_4$, $\text{Hf}(\text{NMe}_2)_4$, $\text{La}(\text{NMe}_2)_3$, $\text{La}(\text{NEt}_2)_3$, $\text{Al}(\text{NMe}_2)_3$, $\text{Al}(\text{NEt}_2)_3$, $\text{Al}_2(\mu\text{-NMe}_2)_2(\text{NMe}_2)_4$, $\text{Y}(\text{NMe}_2)_3$, $\text{Y}(\text{NEt}_2)_3$, $\text{Ti}(\text{NMe}_2)_4$, $\text{Ti}(\text{NEt}_2)_4$, $\text{Ta}(\text{NMe}_2)_5$, $\text{Ta}(\text{NEt}_2)_5$.
36. The CVD precursor composition according to claim 30, wherein the metalloamide source reagent compound is selected from the group consisting of $\text{Zr}(\text{NMe}_2)_4$, $\text{Zr}(\text{NEt}_2)_4$, $\text{Hf}(\text{NEt}_2)_4$ and $\text{Hf}(\text{NMe}_2)_4$.
37. A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including a vapor source reagent mixture including a metalloamide source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, alkylsilyl; x is the oxidation state of metal M.

38. The CVD precursor according to claim 37, wherein the CVD precursor composition further comprises a vapor source reagent compound selected from the group consisting of: silane, trimethylsilane, tetraethylorthosilicate.
39. A CVD precursor composition for forming a thin film dielectric on a substrate, such precursor composition including a vapor source reagent mixture including a metalloamide source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R1 and R2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, alkylsilyl; x is the oxidation state of metal M; and

an aminosilane source reagent compound of the formula:



wherein H is hydrogen; x is from 0 to 3; Si is silicon; N is nitrogen; each of R1 and R2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, and C₁-C₈ perfluoroalkyl.

40. A CVD multi-component, single source reagent composition useful for forming a silicate thin film dielectric on a substrate, the source reagent composition comprising at least one metalloamide vapor source reagent compound of the formula:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R1 and R2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, alkylsilyl; x is the oxidation state of metal M;

at least one aminosilane vapor source reagent compound of the formula:



wherein H is hydrogen; x is from 0 to 3; Si is silicon; N is nitrogen; each of R1 and R2 is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, and C₁-C₈ perfluoroalkyl; and

a solvent medium in which the metalloamide compound and the aminosilane compound are soluble or suspendable.

41. A CVD method of forming a dielectric thin film on a substrate, comprising the steps of:
- vaporizing a source reagent composition comprising at least one metalloamide precursor to form a source reagent precursor vapor;
- transporting the source reagent precursor vapor into a chemical vapor deposition zone, optionally using a carrier gas;
- contacting the source reagent precursor vapor with a substrate in said chemical vapor deposition zone at elevated temperature to deposit a dielectric thin film on the substrate.

42. The method according to claim 41 wherein the metalloamide precursor has the general formula of:



wherein M is selected from the group consisting of: Zr, Hf, Y, La, Lanthanide series elements, Ta, Ti, Al; N is nitrogen; each of R¹ and R² is same or different and is independently selected from the group consisting of H, aryl, perfluoroaryl, C₁-C₈ alkyl, C₁-C₈ perfluoroalkyl, alkylsilyl; and x is the oxidation state of metal M.

43. The CVD method according to claim 42, wherein the source reagent composition is vaporized in a liquid delivery apparatus.

44. The CVD method according to claim 42, wherein the source reagent vapor is transported into the chemical vapor deposition chamber in a pulsed deposition mode.

45. The CVD method according to claim 42, wherein the dielectric thin film is deposited in the absence of an oxidizer.

46. The CVD method according to claim 42, wherein the source reagent vapor further comprises a co-reactive gas.

47. The CVD method according to claim 46, wherein the co-reactive gas is selected from the group consisting of ozone, water vapor and reactive alcohols.

48. The CVD method according to claim 42, wherein the metalloamide source reagent compound is selected from the group consisting of: $\text{Zr}(\text{NMe}_2)_4$, $\text{Zr}(\text{NEt}_2)_4$, $\text{Hf}(\text{NMe}_2)_4$ and $\text{Hf}(\text{NEt}_2)_4$.
49. The CVD method according to claim 42, wherein the metalloamide source reagent compound is $\text{Hf}(\text{NMe}_2)_4$.
50. The CVD method according to claim 49, wherein the metalloamide source reagent compound is dissolved or suspended in octane.
51. The CVD method according to claim 42, wherein the metalloamide source reagent compound is solubilized or suspended in a solvent.
52. The CVD method according to claim 51, wherein the solvent is octane.
53. The CVD method according to claim 42, wherein the metalloamide source reagent compound is $\text{Zr}(\text{NMe}_2)_4$.
54. The CVD method according to claim 53, wherein the metalloamide precursor further comprises $\text{La}(\text{NMe}_2)_3$.
55. The CVD method according to claim 42, wherein the metalloamide source reagent compound is, $\text{Y}(\text{NMe}_2)_3$.
56. The CVD method according to claim 42, wherein the metalloamide source reagent compound comprises $\text{Hf}(\text{N}(\text{CH}_3)_2)_4$ and $\text{La}(\text{N}(\text{CH}_3)_2)_5$.
57. The CVD method according to claim 42, further comprising an aminosilane precursor.
58. The CVD method according to claim 57, wherein the metalloamide source reagent compound is $\text{Hf}(\text{NMe}_2)_4$ and the aminosilane source reagent compound is $\text{Si}(\text{NMe}_2)_4$.

59. The CVD method according to claim 42, wherein the carrier gas is selected from the group consisting of : He, Ar, H₂, and O₂,
60. The CVD method according to claim 42, further comprising an oxidizing gas selected from the group consisting of: O₂, N₂O, NO and O₃.
61. The CVD method according to claim 60, wherein the oxidizing gas is N₂O.
62. The CVD method according to claim 58, further comprising an oxidizing gas, wherein the oxidizing gas is N₂O.
63. The CVD method according to claim 42, wherein the metalloamide source reagent compound is vaporized at temperature in the range of from about 100°C to about 300°C.
64. The CVD method according to claim 42, wherein the chemical vapor deposition zone is at a temperature in the range of from about 350°C to about 750°C.
65. A method of forming a dielectric thin film on a substrate, comprising the steps of:

vaporizing a source reagent precursor composition mixture comprising at least one metalloamide precursor and at least one aminosilane precursor, to form a source reagent precursor vapor;

transporting the source reagent precursor vapor into a chemical vapor deposition zone, optionally using a carrier gas;

contacting the source reagent precursor vapor with a substrate in said chemical vapor deposition zone at elevated temperature, to deposit a dielectric thin film on the substrate.
66. The CVD method according to claim 65, wherein the metalloamide source reagent compound further comprises Zr(NMe₂)₅.
67. The CVD method according to claim 65, wherein the metalloamide source reagent compound is Hf(NMe₂)₄ and the aminosilane source reagent compound is Si(NMe₂)₄.

68. The CVD method according to claim 67, further comprising CVD deposition of a HfN gate conductor on the dielectric thin film from the metalloamide source reagent and a co-reactant gas selected from the group consisting of NH_3 and N_2 plasma.
69. A method of making a gate dielectric and a gate electrode comprising the steps of:
- vaporizing a first precursor composition comprising at least one metalloamide source reagent compound to form a first source reagent precursor vapor;
 - transporting the first source reagent precursor vapor into a chemical vapor deposition zone, optionally using a carrier gas;
 - contacting the first source reagent precursor vapor with a substrate in said chemical vapor deposition zone at elevated temperature to deposit a dielectric thin film on the substrate;
 - vaporizing a second precursor composition comprising at least one metalloamide source reagent compound to form a second source reagent precursor vapor;
 - transporting the second source reagent precursor vapor into a chemical vapor deposition zone, optionally using a carrier gas;
 - contacting the second source reagent precursor vapor with a substrate, comprising the dielectric thin film, in said chemical vapor deposition zone at elevated temperature to deposit a gate conducting thin film on the dielectric thin film.
70. The method of claim 69, wherein the gate electrode is a metal nitride gate electrode.
71. The method of claim 69, wherein the metalloamide source reagent compound is $\text{Hf}(\text{NMe}_2)_4$.
72. The method of claim 69, wherein the first precursor composition further comprises an amino silane source reagent.
73. The method of claim 69, wherein the aminosilane comprises $\text{Si}(\text{NMe}_2)_4$.

74. The method of claim 69, wherein the first source reagent precursor vapor further comprises a process gas.
75. The method of claim 74, wherein the process gas is N_2O .
76. The method of claim 69, wherein the second source reagent precursor vapor further comprises a process gas.
77. The method of claim 76, wherein the process gas is NH_3 .
78. The method of claim 69, wherein the first and second precursor composition comprises $Hf(NMe_2)_4$.
79. A dielectric thin film formed by the method of claim 65.
80. The dielectric thin film according to claim 79, wherein the dielectric thin film is selected from the group consisting of gate dielectrics, high dielectric constant metal oxides, and ferroelectric metal oxides.
81. The dielectric thin film according to claim 79, wherein the dielectric thin film is a metal silicate gate dielectric.
82. The gate dielectric thin film according to claim 79, wherein the dielectric thin film is selected from the group consisting of: $ZrSiO_4$; $HfSiO_4$; $Ta_{1-x}Al_xO_y$, where x is 0.03-0.7 and y is 1.5-3; $Ta_{1-x}Si_xO_y$, where x is 0.05-0.15 and y is 1.5-3; $Ta_{1-x-z}Al_xSi_zO_y$, where $0.7 > x+z > 0.05$, $z < 0.15$ and y is 1.5-3; HfO_2 ; ZrO_2 ; Ta_2O_5 ; $Zr_xSi_{2-x}O_4$ where x is 0.2-1.6; $Hf_xSi_{2-x}O_4$, where x is 0.2-1.6; $Hf_xLa_ySi_{2-x}O_{4+1.5y}$, where x is 0.2-1.6 and y is 0-1; $Zr_xLa_ySi_{2-x}O_{4+1.5y}$, where x is 0.2-1.6 and y is 0-1; $Hf_xAl_ySi_{2-x}O_{4+1.5y}$, where x is 0.2-1.6 and y is 0-0.2; $Zr_xAl_ySi_{2-x}O_{4+1.5y}$, where x is 0.2-1.6 and y is 0-0.2.
83. The gate dielectric thin film according to claim 79, wherein the gate dielectric thin film is selected from the group consisting metal oxide, a metal silicate and metal silicon-oxy-nitride.

84. The gate dielectric thin film according to claim 79, wherein the gate dielectric thin film is a metal silicate gate dielectric thin film.
85. The gate dielectric thin film according to claim 79, wherein the ratio of M_x/Si_{1-x} in the silicate gate dielectric thin film, wherein x is between 0.01 to 10.